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Vibrational analysis of 2-chlorohexane

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Abstract : A detailed analysis of vibrational spectra and assignment of frequencies of 2-chlorohexane liquid with the aid of normal coordinate calculations for its four most probable conformations are reported in the present paper. This has necessitated modifications in many previously suggested assignments such as for those of prominent bands at 1466, 1460, 1445, 1432, 1378, 1346, 1304, 550 and 465 cm^{-1} assigned to the modes CH_2 bend, CH_2 bend, CH_2 bend, CH_3 asym bend, CH_3 sym. bend, CH_3 sym bend, CH_2 wag, ClCH bend and CCC bend respectively. These bands have now been correlated to the CH_2 wag, CH_3 asym bend, CH_3 sym bend, CH_2 wag, CH_2 bend, CH_2 bend, CH_3 sym bend, CCC bend and ClCH bend modes respectively.

Keywords : Infrared and Raman spectra, vibrational analysis, 2-chlorohexane

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Infrared and Raman spectra of 1-chloro-, 2-chloro-, 3-chloro-hexanes in neat liquid and of 1,6-dichlorohexane in liquid as well as solid phases have been published from this laboratory earlier [1]. However, their vibrational analyses were only tentative in the absence of their normal coordinate calculations. Normal coordinate calculations were used by the present authors for interpretation of vibrational analysis of 1-chlorohexane [2], which has been found to exhibit rotational isomerism. Extending the previous studies to 2-chlorohexane, normal coordinate calculations for its four most probable conformations have been shown to explain all the observed frequencies of the molecule for the first time. This has led to modifications in several previously proposed assignments of frequencies of the compound.

Starting with six probable conformers for 2-chlorohexane, namely, I- with all the carbon atoms of the compound in one plane (Figure 1), II and III where CH_3 group attached to C_5 is rotated about the C_4–C_5 bond to occupy the position of H_9 and H_{10} respectively, IV- in which CH_3 group attached to C_2 is rotated about C_2–C_3 bond to go to the position of H_4, while Cl atom coming in the skeletal plane, V and VI- in which CH_3 group attached to C_5 atom takes the position of H_9 and H_{10} respectively, in addition to Cl atom being in the skeletal plane. However, the very strongly observed infrared and Raman frequencies around 615 cm^{-1} and 673 cm^{-1} corresponding to C–Cl stretch mode could be calculated for I, II and III (616 cm^{-1}) and V (666 cm^{-1}) only, suggesting that only these conformers are present in the liquid. Assuming the structure of 2-chlorohexane as shown in Figure 1, the

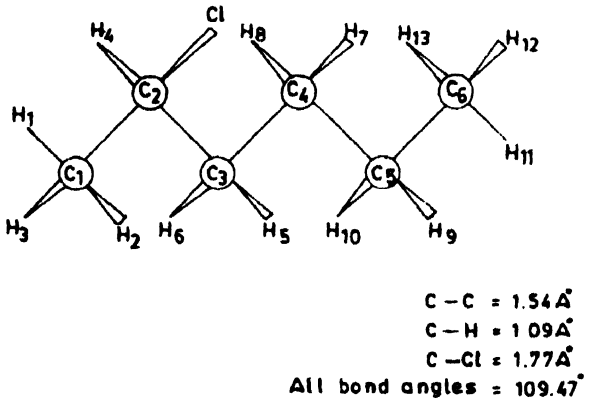

Figure 1. Structure of 2-chlorohexane (I)

normal coordinate calculations were carried out first for this geometry of the molecule by transferring the force field from 2-chloro-4-methylpentane [3] and dimethylhexanes [4]. It was found that most of the calculated frequencies of the conformer I fitted well with the prominent bands of the liquid

phase infrared and Raman spectra of the molecule confirming that it is the most stable conformer. In this, refinement of 18 force constants of the Generalized Valence Force Field (GVFF) were carried out to obtain the best fit of the calculated frequencies with 39 observed bands of the spectra with an average error of 8.2 cm^{-1}. The refined force field was then used to simultaneously calculate the frequencies for all the four conformers and to further refine to fit nearly 60 observed frequencies of the spectra with an approximate error of ~ 6.8 cm^{-1}. The final force field is given in the Table 1. The computational details and the molecular parameters used in the present calculations are the same as described elsewhere [2].

Table 1. Force constants for 2-chlorohexane

Force constants	Group	Coordinate(s) involved	Atoms(s) common	Value[a]
Stretch				
K_r	CH_3	C–H		4 727
K_d	CH_2	C–H		4 541
K_t	C–H	C–H		4 792
K_R	C C	C–C		4 412
K_{Cl}	C Cl	C–Cl		3 438
Stretch-stretch				
F_r	CH_3	CH,CH		0 010
F_d	CH_2	CH,CH		0 009
F_R	C–C C	CC,CC		0 165
$F_{R(Cl)}$	C–C–Cl	CC,CCl		0 691
Bend				
H_a	CH_3	HCH		0 533
H_β	C–CH_3	CCH		0 696
H_α	CH_2	HCH		0 458
H_γ	C–CH_2–C	CCH		0 731
H_ζ	C–CH–C	CCH		0 522
$H_\gamma(Cl)$	C–CHCl–C	CCH		0 694
H_θ	CHCl	ClCH		0 616
H_ω	C–C–C	CCC		1 317
H_Ξ	C–C–Cl	CCCl		1 091
Stretch-bend				
$F_{R\beta}$	C–CH_3	CC,CCH	C–C	0 600
$F_{R\gamma}=F_{R\zeta}$	C–CH_2–C	CC,CCH	C–C	0 510
$F''_{R\gamma}=F''_{R\zeta}$	C CH_2–C	CC,CCH	C	0 034
$F_{R\gamma}(Cl)$ $F_{R\zeta}(Cl)$	C–CHCl–CH_2	CC,CCH	C C	0 315
$F_{R\omega}$ $F_{R\phi}$	C C–C	CC,CCC	C C	0 671
$F_{R\Xi}$	C–C–Cl	CC,CCCl	C–C	–0.226
$F_{Cl\zeta}$	C–CHCl–C	CCl,CCH	C	0 226
$F_{Cl\theta}$	CHCl	CCl,ClCH	C–Cl	0 333
$F_{Cl\omega}$	C CHCl–C	CCl,CCC	C	–0 220
$F_{Cl\Xi}$	C–CHCl–C	CCl,CCCl	C–Cl	0.553
Bend-bend				
F_β	C–CH_3	CCH,CCH	C–C	–0 011
F_γ	C–CH_2–C	CCH,CCH	C C	–0.019
$F''_\gamma=F''_\zeta$	C–CH_2–C	CCH,CCH	C–H	–0 054

Table 1. *(Cont'd)*

Force constants	Group	Coordinate(s) involved	Atoms(s) common	Value[a]
F_ϕ	CC_3	CCC,CCC	C–C	–0.041
$F_{\gamma\omega}=F_{\beta\omega}$	C–CH_2–C	CCH,CCC	C–C	–0 111
F_Ξ	C–CCl C	CCCl,CCCl	C–Cl	–0.007
$F_{\zeta\theta}$	C–CHCl–C	CCCl,ClCH	C–Cl	0 196
f'_γ $f'_{\gamma\beta}$ $f'_{\beta\zeta}$	CH_2 CH_2	HCC,CCH [trans]	C–C	0.127
f^g_γ $f^g_{\gamma\beta}$ $f^g_{\beta\zeta}$	CH_2–CH_2	HCC,CCH [gauche]	C–C	0.118
f''_γ $f''_{\gamma\beta}$ $f''_{\beta\zeta}$	C* CH_2–C*H_2	HCC*,CC*H [trans]	C	0 070
$f^{g'}_\gamma$ $f^{g'}_{\gamma\beta}$ $f^{g'}_{\beta\zeta}$	C*–CH_2–C*H_2	HCC*,CC*H [gauche]	C	0.040
$f'_{\gamma\omega}$ $f'_{\gamma\phi}$	C–CHCl–CH_2–CC_2	CCC,CCH [trans]	C–C	0.049
$f^g_{\gamma\omega}$ $f^g_{\gamma\phi}$ $f^g_{\beta\omega}$	C–CHCl–CH_2–CHC_2	CCC,CCH [gauche]	C–C	–0 052
f'_{ω} $f'_{\omega\phi}$	C C–C–CC_2	CCC,CCC [trans]	C–C	0.146
f^g_{ω} $f^g_{\omega\phi}$	C–C–C–C_2	CCC,CCC [gauche]	C–C	0.011
$f'_{\gamma\Xi}$	CCl CH_2	HCC,CCCl [trans]	C–C	0 041
$f^g_{\gamma\Xi}$	CCl–CH_2	HCC,CCCl [gauche]	C–C	–0.037
$f'_{\omega\Xi}$	C C C–Cl	CCC,CCCl [trans]	C–C	0.067
$f^g_{\omega\Xi}$	C C–C–Cl	CCC,CCCl [gauche]	C–C	0.150
Torsion				
H_τ	C–C	C–C		0 009

[a]Stretching constants are in units of mydn $Å^{-1}$, stretch-bend interaction constants are in units of mdyn rad^{-1}, bending constants are in units of mydn $Å\ rad^{-2}$

All the four conformations of the molecule have the same symmetry C_1 with their vibrational modes belonging to the same species *A* and therefore, are allowed in infrared and Raman both. Accordingly, almost all the prominent bands have appeared in both the infrared and Raman spectra. All these observed bands of the molecule in the infrared and Raman spectra could be correlated with the calculated frequencies for the four conformers and their assignments to various modes of vibration on the basis of potential energy distributions have been given in Table 2. From the Table 2, it is evident that C–H stretch vibrations for all the four conformations lie in the frequency range 2980–2848 cm^{-1} and these are mainly pure modes. The next lower frequencies are calculated for the CH_3 deformation, CH_2 deformation and CH_2 wagging modes in the approximate range 1468–1300 cm^{-1} and have been correlated in most cases to observed bands. The next lower range 1295–1207 cm^{-1} of frequencies consists of CH_2 twisting and CH bend as mixed modes. Below this and upto about 620 cm^{-1} are C–C stretch,

Table 2. Calculated and observed wavenumber and approximate potential energy distribution for 2-chlorohexane

	I		II		III		IV	
Vibrational mode	Calc cm^{-1}	Obs cm^{-1}	Calc cm^{-1}	Obs cm^{-1}	Calc cm^{-1}	Obs cm^{-1}	Calc cm^{-1}	Obs cm^{-1}
CH_3as	2980 (66)	2980 I	2980 (67)	2980 I	2980 (67)	2980 I	2980 (70)	2980 I
CH_3as	2980 (69)	2980 I	2980 (67)	2980 I	2980 (67)	2980 I	2980 (70)	2980 I
CH_3as	2980 (99)	2980 I	2980 (99)	2980 I	2980 (99)	2980 I	2980 (99)	2980 I
CH_3as	2979 (99)	2980 I	2979 (99)	2980 I	2979 (99)	2980 I	2979 (99)	2980 I
CHs	2966 (95)	2965 R	2965 (95)	2965 R	2966 (95)	2965 R	2965 (95)	2965 R
CH_2as	2924 (51)	2930 *	2923 (50)	2930 *	2923 (52)	2930 *	2924 (49)	2930 *
CH_2as	2920 (50)	2915 R	2920 (80)	2915 R	2920 (80)	2915 R	2920 (80)	2915 R
CH_2as	2916 (49)	2915 R	2917 (50)	2915 R	2917 (47)	2915 R	2917 (51)	2915 R
CH_3ss	2870 (99)	2875 R	2870 (99)	2875 R	2870 (99)	2875 R	2870 (99)	2870 R
CH_3ss	2870 (99)	2865 R	2870 (99)	2865 R	2870 (99)	2865 R	2870 (99)	2865 R
CH_2ss	2855 (49)	2860 I	2854 (52)	2860 I	2854 (53)	2860 I	2855 (65)	2860 I
CH_2ss	2851 (49)	2848 R	2852 (94)	2848 R	2852 (94)	2848 R	2852 (92)	2848 I
CH_2ss	2848 (50)	2848 R	2849 (51)	2848 R	2849 (51)	2848 R	2850 (61)	2848 R
$CH_2\omega$	1468 (21)	1466 I	1449 (32)	1445 *	1449 (33)	1445 *	1449 (32)	1445 *
$CH_3a\delta$	1462 (72)	1460 I	1463 (43)	1466 I	1465 (44)	1466 I	1463 (59)	1466 I
$CH_3a\delta$	1461 (55)	1460 I	1462 (50)	1460 I	1461 (51)	1460 I	1462 (65)	1460 I
$CH_3a\delta$	1460 (43)	1460 I	1460 (83)	1460 I	1460 (83)	1460 I	1461 (86)	1460 I
$CH_3a\delta$	1460 (91)	1460 I	1460 (86)	1460 I	1460 (86)	1460 I	1460 (86)	1460 I
$CH_3s\delta$	1442 (47)	1445 *	1443 (45)	1445 *	1453 (23)	1460 I	1452 (30)	1445 *
$CH_2\omega$	1428 (34)	1420 R	1434 (27)	1432 I	1435 (27)	1432 I	1429 (37)	1432 I
$CH_2\omega$	1393 (25)	1381 R	1397 (24)		1397 (23)		1403 (18)	-
$CH_2\delta$	1383 (21)	1381 R	1381 (35)	1381 R	1380 (32)	1378 I	1369 (26)	
$CH_2\delta$	1347 (21)	1346 I	1342 (36)	1346 I	1340 (43)	1346 I	1341 (45)	1346 I
$CH_2\omega$	1319 (44)	1325 I	1329 (48)	1325 I	1333 (47)		1331 (48)	
$CH_3s\delta$	1301 (53)	1304 *	1299 (41)	1304 *	1300 (38)	1304 *	1299 (51)	1304 *
$CH\delta$	1295 (37)	1293 I	1293 (25)	1293 I	1291 (25)	1291 R	1283 (27)	1291 R
$CH\delta$	1270 (59)	1265 R	1269 (63)	1265 R	1270 (62)	1265 R	1255 (33)	
CH_2t	1254 (57)	1262 I	1247 (63)	1246 I	1247 (68)	1246 I	1248 (49)	1246 I
CH_2t	1236 (61)	1240 R	1235 (59)	1240 R	1237 (68)	1240 R	1237 (75)	1240 R
CH_2t	1207 (49)	1205 I	1209 (48)	1208 R	1208 (47)	1208 R	1232 (51)	1240 R
CCs	1144 (40)	1140 I	1145 (35)	1151 *	1145 (41)	1151 *	1143 (47)	1127 I
								1125 R
CH_3r	1079 (63)		1083 (56)	1090 I	1084 (56)	1091 R	1084 (56)	1090 I
CH_3r	1065 (77)	1065 I	1068 (76)	1068 R	1067 (75)	1068 R	1067 (76)	1068 R
CH_3r	1045 (57)	1050 I	1045 (53)	1050 I	1044 (51)	1040 R	1041 (68)	1040 R
				1055 R				
CH_3r	1016 (50)	1018 I	1014 (53)	1018 I	1014 (53)	1018 I	1022 (57)	1020 R
CCs	996 (29)	1000 R	988 (17)	985 I	988 (16)	985 I	973 (24)	973 I
				982 R		982 R		974 R
CCs	939 (52)	950 I	914 (39)	915 I	918 (31)	915 R	903 (38)	905 *
CH_2r	877 (24)	881 I	882 (21)	896 I	871 (25)	872 R	856 (26)	-
				894 R				
CCs	853 (25)	826 R	855 (14)	828 I	860 (34)	-	872 (21)	872 R
CCs	805 (47)	811 I	790 (48)	782 I	792 (44)	790 R	798 (46)	793 I
		813 R						
CH_2r	756 (46)	745 *	738 (52)	735 R	759 (44)		751 (51)	745 *
				730 I				
CH_2r	680 (49)	690 R	714 (40)	-	696 (37)	690 R	705 (41)	

Table 2. *(Cont'd)*

Vibrational mode	I		II		III		IV	
	Calc cm^{-1}	Obs cm^{-1}	Cals cm^{-1}	Obs cm^{-1}	Calc. cm^{-1}	Obs cm^{-1}	Calc cm^{-1}	Obs cm^{-1}
CCls	618 (125)	615 I	618 (123)	615 I	621 (124)	615 I	666 (104)	673 I
		612 R		612 R				672 R
CCCδ	542 (28)	550 I	520 (29)		515 (29)	-	522 (29)	-
		548 R						
CCCδ	438 (19)	427 R	367 (43)	375 R	465 (14)	465 *	449 (33)	440 *
		426 I						
ClCHδ	349 (44)	-	465 (13)	465 *	381 (19)	393 R	354 (42)	365 R
CCCδ	294 (79)	294 R	300 (75)	294 R	300 (73)	294 R	268 (36)	262 R
CCClδ	254 (46)		264 (31)	262 R	255 (21)		332 (37)	338 R
$CH_3\tau$	228 (94)		214 (54)		211 (44)		218 (79)	
CCCδ	134 (44)		161 (40)		162 (41)		133 (42)	
$CH_3\tau$	73 (99)		73 (99)		73 (99)		72 (99)	
CCτ	42 (69)		40 (68)		40 (70)		41 (65)	
CCτ	27 (94)		23 (44)		24 (60)		25 (75)	
CCτ	18 (65)		16 (53)		17 (40)		18 (49)	

Number in parentheses indicates percent potential energy distributions

as = asymmetric stretch, ss = symmetric strech, δ = bend, aδ = asymmetric bend, sδ = symmetric bend,

ω = wagging, r = rocking, τ = torsion, I = Infrared bands, R = Raman bands, * = bands observed in both infrared and Raman spectra

CH_3 rocking, CH_2 rocking and C–Cl stretch modes. The C–Cl stretch frequencies in conformations I-III have been calculated at about 616 cm^{-1}, while in the last conformation this mode has been calculated at about 666 cm^{-1}. This shows a higher value for C–Cl stretch mode in the conformation where Cl atom lies in the skeletal plane, similar to what was observed in 1-chlorohexane [2]. Below 600 cm^{-1} is the range for CCC bend, ClCH bend and CCCl bend. The lowest frequency range consists of torsional modes mainly as pure modes.

There are certain observed bands which could be assigned to only one conformer. While all the most prominent bands observed in infrared and Raman have been assigned to conformer I, some of them are exclusively correlated to this conformer, namely at 1205, 1140, 1065, 881, 811, 550 and 426 cm^{-1} in infrared and at 1420, 1000, 826, 813, 548 and 427 cm^{-1} in Raman. Four infrared bands at 896, 828, 782 and 730 cm^{-1} and five Raman bands at 1055, 894, 735, 375 and 262 cm^{-1} are assigned to conformer II only. Similarly, three Raman bands at 1091, 790 and 393 cm^{-1} are correlated uniquely to conformer III. Further, six infrared bands at 1127, 973, 905, 793, 673 and 440 cm^{-1} and eight Raman bands at 1125, 1020, 974, 905, 672, 440, 365 and 338 cm^{-1} belong to the last conformer only. These observations justify the existence of all the four conformers of the molecule in the liquid phase at ambient temperatures.

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